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Optimization of the growth of the InGaP etch-stop layer by MOVPE for InGaP/GaAs HBT device application

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Abstract

InGaP has high etching selectivity to GaAs. It can be used as the etch-stop layer to easily fabricate the InGaP/GaAs heterojunction bipolar transistors (HBTs). This process will also increase the uniformity and manufacturability of the HBT devices. However, the InGaP etch-stop layer will increase the energy barrier height that electrons have to overcome flowing from the collector to the sub-collector, which will decrease the DC current gain of the device (T. Kobayashi, K. Taira, F. Nakamua, H. Kawai, J. Appl. Phys. 65 (1989) 4898). Therefore, the InGaP etch-stop layer has to be thin enough not to affect the device performance. But the spontaneous formation of the $In_xGa_{1-x}As_yP_{1-y}$ intermixing layer between GaAs/InGaP during the metal organic vapour-phase epitaxy (MOVPE) growth will affect the InGaP layer thickness needed as an effective etch-stop layer. In this paper, very thin InGaP layer was achieved with the suppression of $In_xGa_{1-x}As_yP_{1-y}$ formation by the optimization of the growth temperature and the gas switching sequence time. An effective 20 Å InGaP etch-stop layer was grown at 575 °C with interruption time of 3 s. Both STEM and PL data proved that the intermixing $In_xGa_{1-x}As_yP_{1-y}$ layer was eliminated and from the selective etching experiment, this 20 Å InGaP layer can stand 45 s etching by the H_3PO_4:H_2O_2:H_2O = 1:1:20 solution.

Keywords: A1. Photoluminescence; A1. Transmission electron microscopy; A3. Metal organic vapour-phase epitaxy; B1. InGaP etch-stop layer; B1. $In_xGa_{1-x}As_yP_{1-y}$ intermixing layer; B3. Heterojunction bipolar transistors

1. Introduction

In recent years, InGaP/GaAs heterojunction bipolar transistors (HBTs) have become very popular and are considered as replacements for widely used AlGaAs/GaAs HBTs due to a number of advantages [2]. These advantages include low surface recombination velocity, large valance band offset between InGaP/GaAs, high etch selectivity, lack of DX center problem, and long-term reliability improvement. In the InGaP/GaAs HBTs, InGaP is often used as the etch-stop layer between GaAs collector and subcollector layers due to the fact that InGaP has high etching selectivity to GaAs. The etch-stop layer is used to enhance the reproducibility and manufacturability of the process. However, for the fabrication of the InGaP/GaAs HBTs, the InGaP etch-stop layer between collector and subcollector will increase the energy barrier height that electrons have to overcome flowing from the collector to the sub-collector, which will decrease the DC current gain of the device [1]. Therefore, the InGaP etch-stop layer has to be thin enough not to affect the device performance. But the spontaneous formation of the $In_xGa_{1-x}As_yP_{1-y}$ intermixing layer between GaAs and InGaP usually sacrifice the effective thickness of the InGaP etch-stop layer. It has been speculated that the interfacial layer was formed either by the displacement of P by As when arsine was introduced into the metal organic vapour-phase epitaxy (MOVPE)

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system to grow GaAs or by the In memory effect and the intermixing of AsH_3 and PH_3 gases during the gases switching period in the reactor. Therefore, as GaAs is grown on InGaP, the formation of the intermixing $In_xGa_{1-x}As_yP_{1-y}$ layer is spontaneous. It was reported that the intermixing layer between InGaP/GaAs could be partially solved by shortening the mixing time of PH_3 and AsH_3 to 0.2 s [3]. In this work, it found that the displacement of P by As and the intermixing of AsH_3 and PH_3 gases during the gases switching period can be solved by decreasing the growth temperature of the GaAs cap layer and optimizing the interruption time. At the growth temperature of 575 °C and with the interruption time of 3 s, an 800 Å GaAs cap layer was grown on a 20 Å InGaP layer without intermixing layer. The experimental data show that the interface of GaAs/InGaP was very sharp. Because of formation of InGaAsP interlayer was suppressed, the etching selectivity of thin InGaP layer is very good. In this paper, we will present these experiments and give detailed discussions of these results.

2. Experimental procedure

In this work, the GaAs/InGaP/GaAs heterostructure was grown by MOVPE method at 40 Torr reactor pressure at different growth temperatures and with different gas switching sequence times. The triethyl gallium (TEGa) and trimethyl indium (TMIn) were used as the III source, and the arsine (AsH_3) and phosphine (PH_3) were used as the V source. V/III ratio was kept at 80 for InGaP and 60 for GaAs. Under these conditions, the growth rate was controlled at 25 Å/s. All the growth experiments were done on the (0 0 1) GaAs substrates. The lattice constants of the heterostructures were checked by double crystal X-ray measurements. Photoluminescence (PL) was excited by 532 nm line of the laser, dispersed with a 0.67 m monochromator and detected with cooled photomultiplier tube detector. Phase-sensitive detection of the PL was performed using a lock-in amplifier. Measurements were normally done at 10 K using a closed-cycle helium refrigerator. The TEM samples were prepared using the standard 'sandwich' technique followed by ion milling. Structural analyses of the epitaxial layers were performed on the cross-section by high-resolution transmission electron microscope (HRTEM). This study was carried out on a Phillips-200 electron microscope operating at 200 kV with an interpretable resolution of 0.16 nm. The localized spatial information from HRTEM micrographs was obtained by digital diffractograms (DDFs). The method was based on the measurements of the interplanar spacing in reciprocal space and can be used to determine the frequency and amplitude of the lattice images. Image simulation was performed using the Cerius simulation program.

The experiments in this work are composed of two parts. The first part studies the suppression of the $In_xGa_{1-x}As_yP_{1-y}$ intermixing layer by growing GaAs cap layer at low growth temperature and shortening the gas switching sequence time. Following growth of an InGaP etch-stop layer, a set of GaAs cap layers were grown at different temperatures (575, 600, 625 and 650 °C) with different interruption times (0, 1, 3, 5 and 10 s) and the V/III ratio was controlled in the range of 80 (see Fig. 1), the lattice mismatches and compositions were derived from the X-ray diffraction rocking curves. All samples showed mismatch ($\Delta a/a$) less than 5×10^{-3}, and can be considered as having the same composition. The abruptness and the flatness of the heterointerfaces were precisely estimated through the PL measurement of the InGaP/GaAs samples. A transit layer with As/P exchange has been reported to form during the gas-switching period [5]. This transit layer causes the PL peak of InGaP to disappear, and leads to the appearance of a strong PL peak from itself with a wavelength longer than that of GaAs. From the PL measurements, different InGaAsP peaks were observed for the samples grown at different temperatures and with different interruption times. The interfaces between GaAs and $In_xGa_{1-x}As_yP_{1-y}$ were observed by high resolution TEM and STEM.

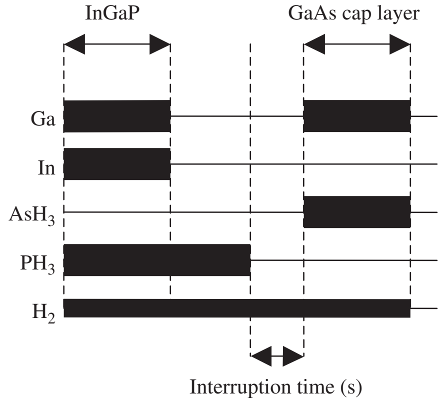

Fig. 1. Gas switching sequence of the source valves for samples grown in this work.

The second part of this work focuses on the studies of the effectiveness of the InGaP etch-stop layer. Etching the InGaP layer using (H_3PO_4:H_2O_2:H_2O = 1:1:20) solution did the work. From the selective etching experiment, it was found that the 20 Å InGaP layer grown could stand 45 s etching by the above solution.

3. Results and discussion

3.1. Dependence of the $In_xGa_{1-x}As_yP_{1-y}$ layer thickness on the growth temperature of the GaAs cap layer on InGaP

The samples grown have two kinds of interfaces, namely GaAs-to-InGaP (normal interface) and InGaP-to-GaAs (inverted interface). The growth of the abrupt GaAs/InGaP heterointerfaces by MOVPE was proved difficult due to the interfacial $In_xGa_{1-x}As_yP_{1-y}$ formation either through the displacement of P by As when arsine is introduced into the MOVPE system to grow GaAs or through the In memory effect and the intermixing of the AsH_3 and PH_3 gases during the gas switching period in the reactor [6]. The thicknesses of the GaAs and InGaP layers were 80 and 800 nm, respectively. In these samples, the GaAs and InGaP layers act as the confining layers for the intermediate $In_xGa_{1-x}As_yP_{1-y}$ layer, thus most of the holes and electrons will recombine within the spontaneously formed $In_xGa_{1-x}As_yP_{1-y}$ layer to provide the observed long-wavelength PL. Fig. 2 shows the low-temperature PL spectra of the GaAs cap grown at different temperatures with the same gas interruption time of 1 s before the GaAs layer growth. The observed long-wavelength PL peaks in the samples come from the $In_xGa_{1-x}As_yP_{1-y}$ layer that formed at the inverted (InGaP-to-GaAs) interface, as observed by Guimaraes [8]. The growth process was usually interrupted when one group-V source was purged before the following group-V source was introduced. Such a gas exchange lead to the As/P intermixing phenomenon at the interfaces, which was caused by the As/P replacement at the interface or the insufficient purge of the previous group-V species. The dominant long wavelength PL peak observed at 862–914 nm is related to the spontaneous $In_xGa_{1-x}As_yP_{1-y}$ layer. The weak PL features at 820 and 832 nm are related to the GaAs material. The faint PL peak at 644 nm is related to the InGaP layer. The formation of the $In_xGa_{1-x}As_yP_{1-y}$ layer was undesired and the thickness of this layer was about several nanometers. The trapping of the carriers by the $In_xGa_{1-x}As_yP_{1-y}$ will suppress the PL peaks of the GaAs and InGaP layers [1]. The PL peak intensities of the GaAs and InGaP layers become weaker, and the $In_xGa_{1-x}As_yP_{1-y}$ peak has a red-shift when the growth temperature of the GaAs cap layer varies from 650 to 575 °C as seen in Fig. 2. The ratio of the InGaAsP PL intensity ($I_{InGaAsP}$) over the InGaP PL intensity (I_{InGaP}) indicates the carriers trapped by the InGaAsP well. Higher $I_{InGaAsP}/I_{InGaP}$ PL ratio for the 650 °C sample proves that the $In_xGa_{1-x}As_yP_{1-y}$ layer formed at 650 °C has the highest As composition. This is due to that the $In_xGa_{1-x}As_yP_{1-y}$ layer with highest As composition has the highest energy band gap, which results in the most obvious PL peak red-shift, and the greatest possibility to trap the electrons from the InGaP/GaAs layers. For the InGaP layer grown at 650 °C, the PL peak intensities of the InGaP/GaAs layers were the weakest among all the samples grown, because most of the electrons were absorbed by the $In_xGa_{1-x}As_yP_{1-y}$ layer. On the contrary, when the GaAs cap layers was grown at 575 °C, the PL peak of the $In_xGa_{1-x}As_yP_{1-y}$ layer has the smallest red-shift, and the PL peak intensities of GaAs and InGaP were the strongest. It suggests that the As atoms can easily replace P atoms on the InGaP surface at high temperature when the sample was exposed to the As vapor during the gas-switching period. That is, the $In_xGa_{1-x}As_yP_{1-y}$ intermixing layer was easier to form at higher temperature growth [6–12]. In this work, the optimized growth temperature of the GaAs cap layer was 575 °C, because the As/P exchange on the surface was well suppressed at this temperature. Fig. 3 is the TEM bright field image of the sample grown at 625 °C. There is an obvious inter-layer between GaAs and InGaP layers in this figure. This layer is the intermixing $In_xGa_{1-x}As_yP_{1-y}$ layer with non-uniform thickness about 5–10 nm. The InGaAsP layer was double checked by STEM image. Fig. 4(a) is the STEM image of the sample grown at 625 °C. The STEM image is

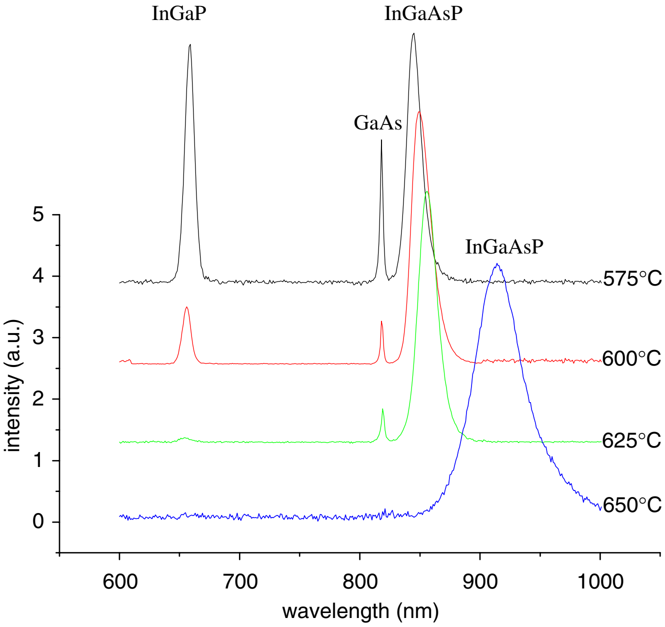

Fig. 2. The low-temperature PL spectra of the GaAs/InGaP/GaAs samples with GaAs cap layer grown at different temperatures.

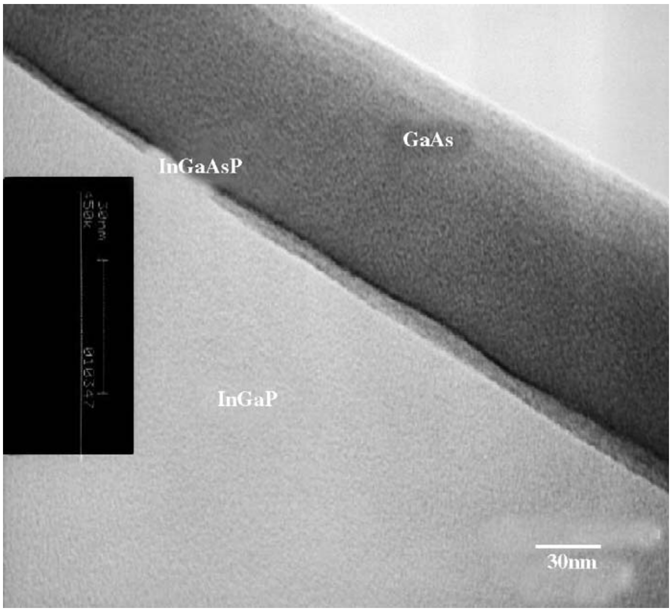

Fig. 3. The TEM bright field image of the sample with GaAs cap layer grown at 625 °C. The spontaneous formation of the InGaAsP intermixing layer between GaAs/InGaP is clearly shown. $In_xGa_{1-x}As_yP_{1-y}$ layer has a non-uniform thickness about 2–5 nm.

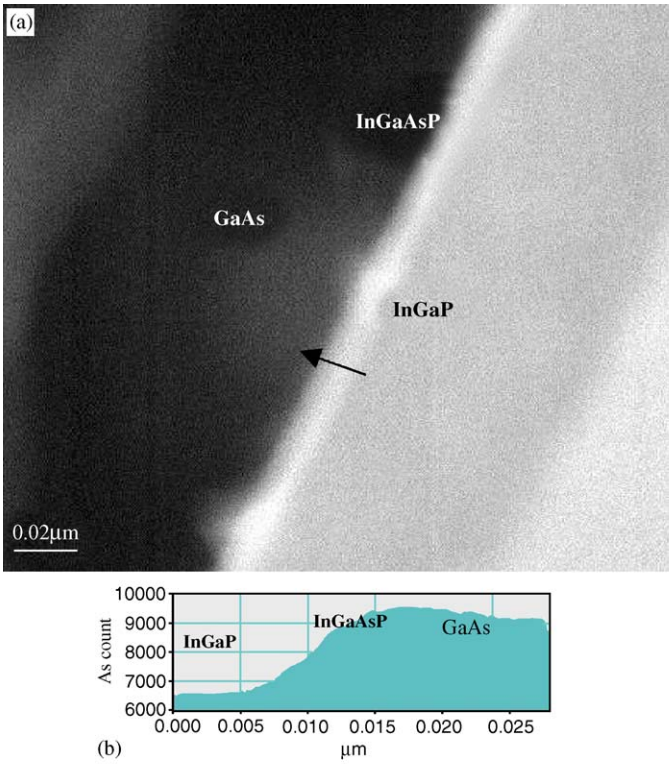

Fig. 4. (a) STEM image of the $In_xGa_{1-x}As_yP_{1-y}$ intermixing layer with thickness about 10 nm. (b) The composition profile across the interface for the sample.

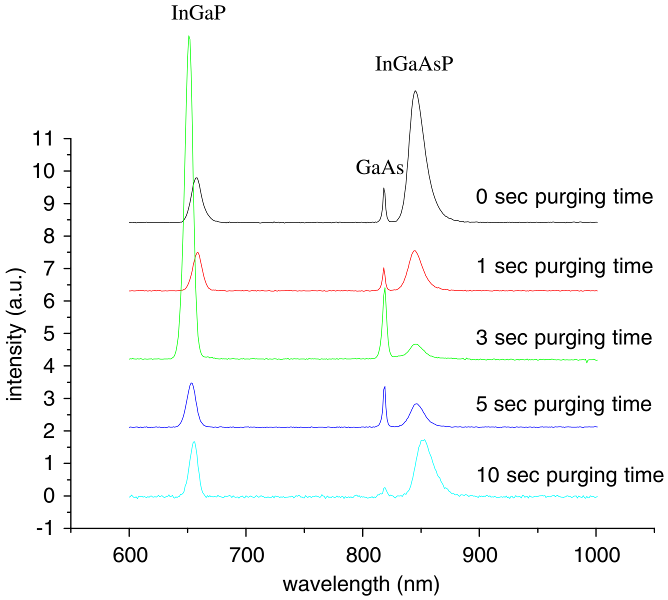

Fig. 5. 10 K PL spectrums of the samples grown at 575 °C with different interruption time.

advantageous for dealing with the thickness of the specimen because the chromatic aberration which can limit the TEM images.

Fig. 4(a) is the STEM image of the sample grown at 625 °C. The $In_xGa_{1-x}As_yP_{1-y}$ intermixing layer with thickness about 10 nm is shown clearly in the picture. Fig. 4(b) shows the distance versus counts to represents the composition profile across the interface of GaAs/InGaP. Three distinct regions are clearly shown in Fig. 4(b), they are GaAs cap layer, intermixing $In_xGa_{1-x}As_yP_{1-y}$ layer and InGaP layer, respectively.

3.2. $In_xGa_{1-x}As_yP_{1-y}$ thickness variation with the interruption time between GaAs and InGaP growth

After the GaAs cap growth temperature was optimized and set at 575 °C, different interruption times such as 0, 1, 3, 5 and 10 s between the growth of the InGaP layer and the growth of the GaAs cap layer were tried. Fig. 5 is the PL intensity verse wavelength for the five samples grown with the different interruption times. The intermixing of the PH_3 and AsH_3 gases during the gas-switching period in the reactor can also affect the $In_xGa_{1-x}As_yP_{1-y}$ layer formation at the GaAs/InGaP interface. By increasing the interruption time, the $In_xGa_{1-x}As_yP_{1-y}$ layer formation can also be suppressed, because the chance for gas intermixing is reduced. According to Nakano's study, when the interruption time of 0.2–1.0 s was used when the sample was grown at 660 °C, the complete P desorption from the InGaP surface was achieved [11]. In these experiments, the InGaP layer was grown at 650 °C first, and then the GaAs cap layer was grown at 575 °C, the interruption time corresponding to the complete P desorption was different from Nakano's study. The abruptness of the heterointerface was estimated through the measurement of the peak intensity of the $In_xGa_{1-x}As_yP_{1-y}$ layer formed at the GaAs/InGaP interface. For the sample grown with the interruption time of 3 s, the PL peak intensity of the $In_xGa_{1-x}As_yP_{1-y}$ layer was very weak as can be seen in Fig. 5. However, the intensity of the $In_xGa_{1-x}As_yP_{1-y}$ peak of the sample with 10 s interruption time was stronger than that of the sample grown with 3 s interruption time. This is due to the over-desorption of the phosphous atoms from the InGaP surface when the interruption time was too long, although the longer the interruption time, the less intermixing of the PH_3 and AsH_3 gases in the reactor. The P atoms desorp easily at high temperatures. For the longer purging time case more P atoms will desorp during the purging period, as we start to grow the GaAs layers, As atoms will replace P atoms desorbed and thicker InGaAsP layer will form. Therefore, the $In_xGa_{1-x}As_yP_{1-y}$ layer grown with longer purging time has higher As composition and results in the peak shift to lower energy side. In this work, it was found that the optimized interruption time for suppressing the $In_xGa_{1-x}As_yP_{1-y}$ formation was 3 s when the GaAs cap layer was grown at a low growth temperature of 575 °C. Fig. 6(a) shows the STEM image of the sample grown with no interruption time. There was an obvious $In_xGa_{1-x}As_yP_{1-y}$ intermediate layer with thickness about 5 nm. Fig. 6(b) shows its composition profile across the interface of GaAs/InGaP. Three regions were clearly

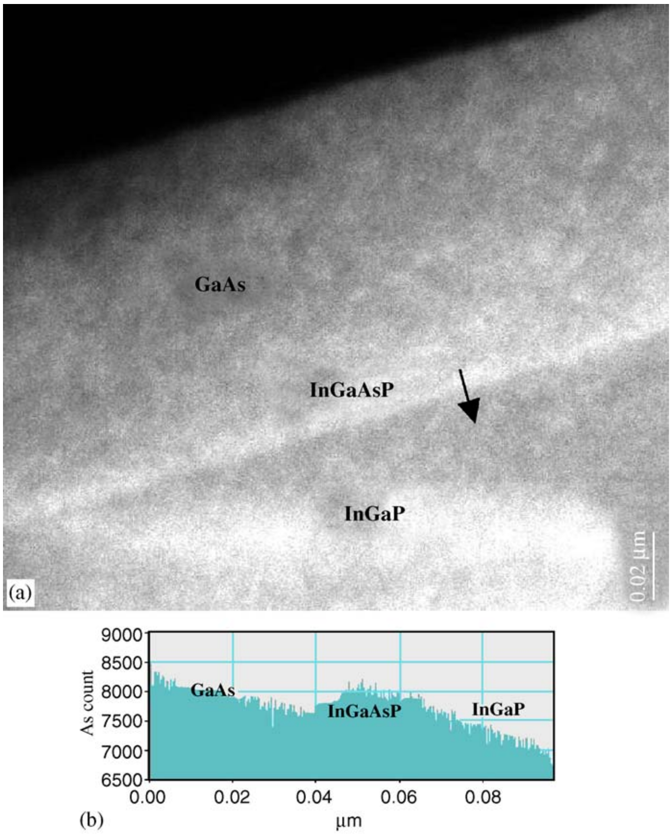

Fig. 6. (a) STEM image of the sample grown without interruption time. The $In_xGa_{1-x}As_yP_{1-y}$ intermixing layer thickness is about 5 nm. (b) The composition profile across the interface of GaAs/InGaP for the same sample.

shown in this figure. They are GaAs cap layer, $In_xGa_{1-x}As_yP_{1-y}$ interlayer and InGaP underlying layer, respectively. In this case, because the PH_3 gas was not purged before AsH_3 gas was introduced into the reactor, the AsH_3 and PH_3 mixed in the reactor and caused a spontaneous $In_xGa_{1-x}As_yP_{1-y}$ layer formation. Fig. 7(a) shows the STEM image of the sample grown with 3 s interruption time. No $In_xGa_{1-x}As_yP_{1-y}$ layer between InGaP/GaAs was observed. Fig. 7(b) shows its composition profile across the interface of the GaAs and InGaP layers. The composition change across the InGaP/GaAs interface was quite abrupt. This means that the PH_3 and AsH_3 mixing can be avoided using 3 s interruption time, and the formation of the $In_xGa_{1-x}As_yP_{1-y}$ layer can be suppressed. Both the PL measurement data and the TEM cross-section images prove that the spontaneously formed $In_xGa_{1-x}As_yP_{1-y}$ layer was suppressed and the abruptness of the GaAs/InGaP interface was improved by the use of the optimized gas-switching sequence.

3.3. *Examination of the InGaP etch-stop layer*

After optimizing the growth temperature of the GaAs cap and the interruption between the growth of the layer the InGaP/GaAs cap, the InGaP layer was grown with different thickness as the etch-stop layer between the GaAs cap layer and the GaAs buffer layer. The selective etch between GaAs/InGaP layers was done by using H_3PO_4:H_2O_2 :H_2O = 1:1:20 solution. The etching rate of GaAs by this solution was about 40 Å/s. The InGaP layer

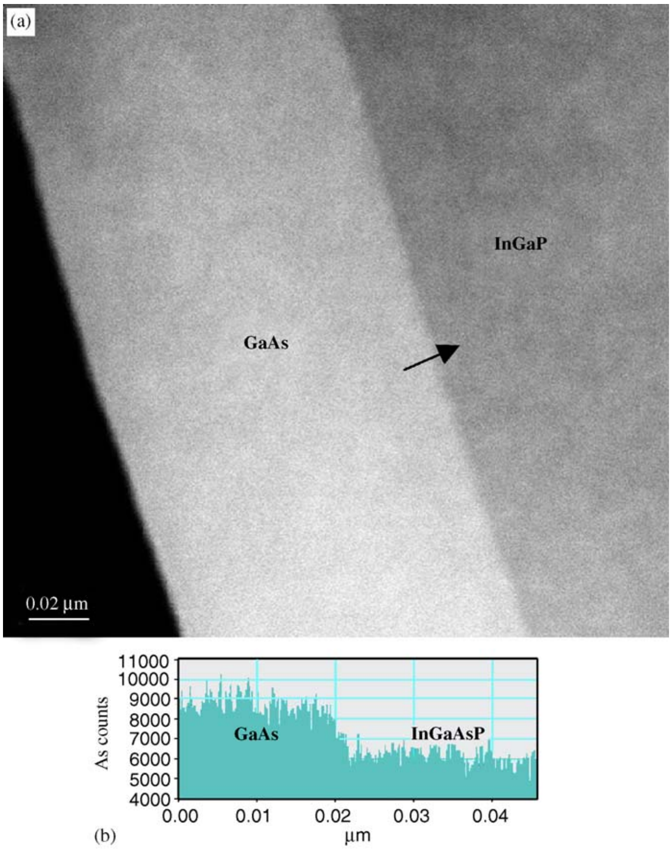

Fig. 7. (a) The STEM image of the sample with 3 s interruption time. No clear $In_xGa_{1-x}As_yP_{1-y}$ intermediate layer between InGaP/GaAs is observed. (b) The composition profile across the interface of GaAs/InGaP for the same sample.

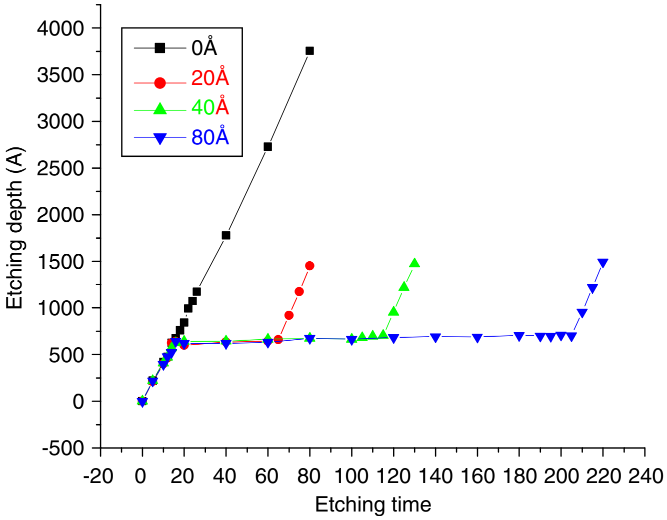

Fig. 8. The etching depth vs. etching time for the samples with different InGaP layer thickness.

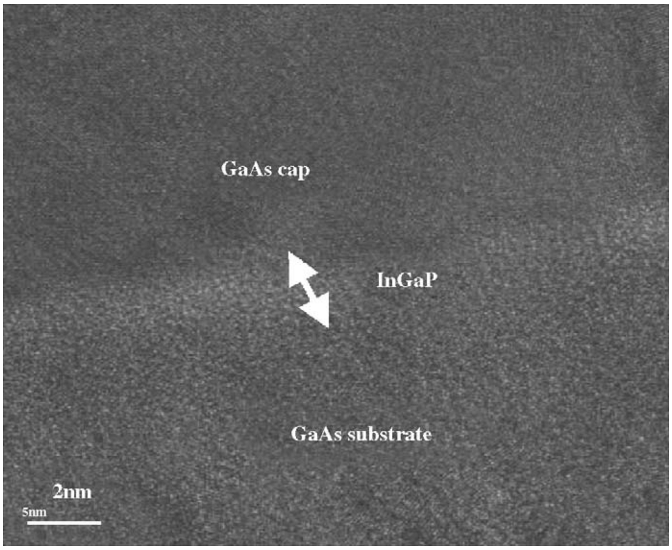

Fig. 9. TEM image of the 2 nm InGaP layer grown on the GaAs substrate with GaAs cap layer on the top.

thicknesses for the samples used for test were 20, 40 and 80 Å. Fig. 8 shows the etching depth verse etching time. The sample without InGaP etch-stop layer was also etched for comparison with other samples. Fig. 9 is the TEM micrograph showing the cross section of the 20 Å InGaP etch-stop layer between the GaAs cap and the GaAs substrate. From the data in Fig. 8, it can be found that the etching process stopped after 20 s etching for all the samples, and the etch-stop period increases with the thickness of the InGaP layer. The sample with 20 Å InGaP etch-stop layer can stand etching for 45 s; meanwhile the sample with 40 Å InGaP etch-stop layer can stand etching for 90 s. Thus, with proper design of the process, a 20 Å InGaP etch-stop layer can be practically used for the HBT device fabrication.

4. Conclusions

In this paper we have shown that, by reducing the growth temperature of the GaAs cap layer to 575 °C and optimizing the interruption time during the gas-switching period to 3 s, the mixing of PH_3 and AsH_3 and the P/As atom replacement on the InGaP surface were both suppressed. Both PL measurement data and TEM cross-section image proved that the spontaneously formed InGaAsP layer almost disappeared and the abruptness of the GaAs/InGaP interface was very sharp. Using the optimized growth temperature of 575 °C and the optimized interruption time of 3 s for the growth of the GaAs cap layer, the InGaP etch-stop layer with 20 Å thickness was successfully achieved without the intermixing $In_xGa_{1-x}As_yP_{1-y}$ layer. It was found that the 20 Å InGaP layer was able to stand the H_3PO_4:H_2O_2:$H_2O = 1:1:20$ solution etches for 45 s. These results show that by optimizing the growth conditions, 20 Å InGaP etch-stop layer can be successfully grown between GaAs cap layer and GaAs bottom layer without the formation of the InGaAsP intermixing layer, and this technique can be used for the design and fabrication of the high-performance HBTs and HEMTs.

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Further reading

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